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BIODIESEL PRODUCTION FROM VEGETABLE OILS: AN OPTIMIZATION PROCESS

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ABSTRACT

Biodiesel production has received considerable attention in the past as a biodegradable and non polluting fuel. The production of biodiesel by transesterification process employing alkali catalyst has been industrially accepted for its high conversion and reaction rates. The use of methoxide as a catalyst to perform the transestirification reaction into biodiesel in this work. The effect of the most relevant variables of the process such as reaction temperature, molar ratio between alcohol and oil, amount of catalyst and amount of free fatty acids fed with oil have been analyzed for this purpose, an ideal sunflower oil using lauric acid and palm oil, coconut oil also used. The alcohol used was methanol. Fats and oils are chemically reacted with alcohol to produce chemical compounds known as fatty acid methyester (Biodiesel). Glycerol, used in pharmaceuticals and cosmetics industry along with many other applications, is produced in this reaction as a product. The cost of biodiesel, however, is main hurdle in commercialization of the product. The used cooking oil as raw material, adoption of batch transesterification process and recovery of high quality glycerol from biodiesel product stream are primary option to be considered to lower the cost of biodiesel.

There are four primary ways to make biodiesel, direct use and blending, micro emulsions, thermal cracking and transesterification. Transesterification reaction is effected by molar ratio of glycerides to alcohol, catalyst, reaction temperature, reaction time and free fatty acids water content of oils or fats .the process of transesterification and its downstream operations also addressed. The transesterification of free fatty acid using this homogeneous catalyst appears as a great alternative and producing high conversion around 98.2%.

KEYWORDS: Biodiesel, Glycerin, Vegetable Oils, Ethanol, Methanol, KOH and NaOH

INTRODUCTION

Biodiesel has gained importance in the recent past for its ability to replace fossil fuels which is likely to run out within a century. The environmental issues concerned with the exhaust gases emission by the usage of fossil fuels also encourage the usage of biodiesel which has proved to be eco friendly far more than fossil fuels.

Biodiesel is known as a carbon neutral fuel because the carbon present in the exhaust was originally fixed from atmosphere. Biodiesel is a mixture of monoalkylesters obtained from vegetables oils like soybean oil, jatropha oil, rapseed oil, palm oil, sunflower oil corn oil, peanut oil, canola oil and cotton seed oil[1]. Apart from vegetable oils, biodiesel can also produced from other sources like animal fat(beef tallow, lard), waste cooking oil, greases

(trap grease, float grease) and algae[2]. A method utilizing all the above mentioned sources was patented by Fogila et.al (1998) [3]. And claiming process to be a cost effective one as it uses inexpensive feedstock. The direct use of vegetable oils as a biodiesel is possible by blending with conventional diesel fuels in a suitable ratio and these esters blends are stable for short term usages. The blending process is simple which involves mixing alone and hence the equipment cost is low. But direct use of these tryglyceric esters (oils) is unsatisfactory and impractical for long term usages in the available diesel engines due to high viscosity, acid contamination and free fatty acid formation resulting in the gum formation by oxidation and polymerization and carbon deposition .Hence vegetables oils are processed so as to acquire properties (viscosity and volatility) similar to that of fossil fuels and the processed fuel can be directly used in the diesel engines available. Biodiesel is a mixture of mono-alkyl esters obtained from vegetable oils like soybean oil, jatropha oil, rapeseed oil, palm oil, sunflower oil, corn oil, peanut oil, canola oil and cottonseed oil. Biodiesel is a mono alkyl ester of long chain fatty acids derived from the renewable lipid feed stock such as vegetable oil or animal fat [4]. Bio represents its renewable and bio-logical source in contrast to traditional problem based on fuel. Diesel refers to its use in diesel engines. As an alternative fuel, bio-diesel can be used in neat form or mixed with petroleum based diesel.

- It is renewable fuel that can be derived from soybean oil, vegetable oils and animal fats. Used cooking oil can even be recycled to produce the fuel.
- It is domestic product that lessens the dependence on foreign oil and produces jobs for the economy.
- It work with the current diesel infrastructure with basically no modification because it posses similar properties to petroleum diesel.
- It can be blended with petroleum diesel in different amounts the most common blend is B20 (20% bio-diesel and 80% petroleum) neat bio-diesel is 100% biodiesel.
- Biodiesel and Biodiesel blend have excellent lubricity properties, which reduces wear on engines.
- It is biodegradable, non toxic, and it is safe to handle.

Biodiesel has a relatively high flash point (150^0C), which makes it less volatile and safer to transport or handle than petroleum diesel. In brief these merits of biodiesel make it good alternative to petroleum based fuel and have led to its use in many countries, especially in environmentally sensitive areas. Due to the increase in the price of the petroleum and the environmental concerns about pollution coming from the car gases, biodiesel is becoming a developing area of high concern. There are different ways of production, with different kinds of materials: refine crude or frying oils. Also there are different types of catalyst, basic ones such as sodium or potassium hydroxides, acids such as sulfuric acid, ion exchange resins, lipases and supercritical fluids. One of the advantages of this fuel is that the raw materials used to produce that are natural and renewable. All these types of oils come from vegetables or animal fat, making it biodegradable and nontoxic. Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from diesel injector. The viscosity of fatty acid methyl ester can go very high levels and it is important to control.

Biodiesel production was studied in 1999 by Milford A. Hanna et.al., [8] and Anjana Srivasta and Ram Prasad [10] studied on Triglycerides – based diesel fuel in 2000., Bio-diesel production from high FFA rubber seed oil was studied by A.S. Ramadhas, S. Jayaraj, C. Muraleedharan in 2004., [13].Heterogeneous esterification of oil with high amount of free fatty acids is studied by J.M. Marchetti and V.U. Miguel in 2006.,[5]. Alok Kumar Tiwari & Hifjur

Raheman reported that Bio-diesel production from jantropha oil (jantropha curcas) [18] with high free fatty acids in 2007: An optimized process. An overview of enzymatic production of biodiesel was studied by Karuppan Muthukumar and Srinivasan Lakshmi Narasimhan in 2007[19] and reported that Biodiesel production has received considerable attention in the recent past as a biodegradable and nonpolluting fuel.

The plant oils usually free fatty acids, Phospho lipids, sterols, water odorants and other impurities, Because of the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification mainly Bio-diesel production can be done through four ways. There are

- Direct use and blending.
- Thermal heating or Pyrolysis.
- Micro emulsions.
- Transesterification.

Direct Use and Blending: Beginning in 1980, there was considerable discussion regarding use of vegetable oil as a fuel. Bartholomew (1981) [22] explained the concept of using food for fuel, indicating that petroleum should be the “alternative” fuel combustion Polyunsaturated fatty acids were very susceptible to polymerization and gum formation caused by oxidation during storage or by complex oxidative and thermal polymerization at the higher temperature and pressure of combustion. The advantages of vegetable oils as diesel fuel are Liquid nature portability, Heat content (80% of diesel fuel), Ready availability and Renewability.

The Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. The problems include are Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, Carbon deposits, Oil ring sticking and Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils.

Pyrolysis: Pyrolysis refers to chemical change caused by application of heat to get simpler compounds from a complex compound. The process is also known as cracking. Vegetable oils can be cracked to reduce viscosity and improve cetane number. The products of cracking include alkanes, alkenes, and carboxylic acids. Soybean oil, cottonseed oil, rapeseed oil and other oils are successfully cracked with appropriate catalysts to get biodiesel [23]. By using this technique good flow characteristics were achieved due to reduction in viscosity. Disadvantages of this process include high equipment cost and need for separate distillation equipment for separation of various fractions. Also the product obtained was similar to gasoline containing sulfur which makes it less eco-friendly [23].

Micro Emulsions: Micro emulsification is another technique that has been reported to produce biodiesel and the components of a bio-diesel micro emulsion include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions [23]. Alcohols such as methanol, ethanol and propanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers. To solve the problems of high viscosity of vegetable oils, micro emulsions, with solvents such as methanol, ethanol has been studied. A microemulsion is defined as colloidal equilibrium dispersion of fluid microstructures. They can improve spray characteristics. All micro emulsions met the maximum viscosity requirement. Methanol was often used due to its economic advantage over ethanol.

Transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. To make it possible, a catalyst is added to the reaction. Transesterification or alcolysis is the displacement of alcohol from an ester in a process similar to hydrolysis, except than alcohol is used instead of water. The process has been widely used to reduce the high viscosity of triglycerides. The transesterification process can be done in a number of ways such as using an alkali catalyst, acid catalyst, biocatalyst, heterogeneous catalyst or using alcohols in their supercritical state. Types of catalyst are Alkali catalyst (Methanol, Ethanol and Butanol), Acid catalyst (H_2SO_4) and enzymatic catalyst (lipase).

The general reaction is Vegetable oil + methanol ------->^{catalyst} Biodiesel +Glycerol.

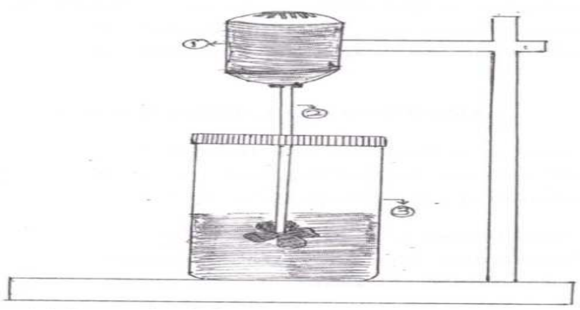
The production of bio-diesel or alkyl ester is well known. There are three basic routes to ester production from oil and fats:

- Based catalyzed transesterification of oils with methanol.
- Direct acid catalyzed esterification of the oil with methanol.
- Conversion of oil to fatty acids, and then to alkyl ester with acid catalysis.

The majority of the alkyl ester produced today is done with based catalyzed reactions because it is most economic for several reasons. Those are Low temperature (150^0C) and pressure (20 psi) processing, high conversion (98%) with nominal side reactions and reaction time, direct conversion to methyl ester with no intermediate steps and Exotic materials of construction are not necessary.

MATERIALS AND METHODS

Experimental Procedure



1. Electrical Motor 2. Stirrer 3. Cylindrical Vessel

Figure 1: Experimental Setup for Production of Biodiesel

The apparatus used in this experiment is as shown in figure 1. One liter cylindrical jar connected with a stirrer which is tightly corked, Thermometer, Measuring jars, Heater and Electrical balance and Experiments were conducted with different oils with NaOH and KOH catalysts to produce biodiesel with methanol in batch process of 250 ml of oil. In this experiment different oils sunflower oil ground nut oil, palm oil and coconut oil are used.

Methoxide Preparation: From standard literature for 1 litre of vegetable oil 220ml of methanol is to be mixed with the amount of catalyst we determined in the titration. Put this in a glass jar or bottle that can be corked well. This mix is called methoxide. If NaOH is the catalyst then it is called as sodium methoxide solution and If KOH is the catalyst then it is called as potassium methoxide solution.

Titration Solution Composition: Sample solution (Methyl ester), Ethanol, Diethyl ether, Phenolphthalein indicator and Titrant 0.02N KOH.

Titration Procedure:-a = V *1000 * PM * C / Mg (1)

$X_{ffa} = a_i - a_t / a_i$ (2)

Titration FFA → EE.

Where FFE =Free fatty acid, EE =Ethyl ester, PM =Molecular weight of mixture, Mg =weight of sample, V =volume of mixture, C =concentration of sample, a_i = the initial acidity of the mixture, a_t = acidity at time t.

The most relevant variables whose effect was studied are: Reaction temperature, ratio of alcohol to mix, amount of catalyst due to the amount of refined oil, types of catalyst and amount of initial free fatty acids.

RESULTS AND DISCUSSIONS

Transesterification reaction readings to the formation of biodiesel are studied by varying Oil content from 150 to 350ml in 50 ml increment, alcohol content from 40 to 60 ml in 10ml increment, Suitability of catalyst - NaOH /KOH, amount of catalyst from 0.9 to 1.2 gm in 0.1 increment, reaction temperatures of 45, 75 and 90°C, reaction time of 20, 40 and 60 min and Suitability of various vegetables oils.

Effect of Oil Content

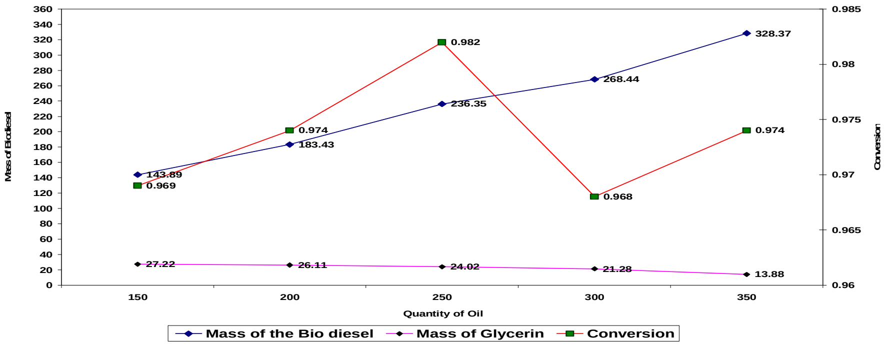


Figure 2: Quality of Oil vs Mass of Biodiesel, Mass of Glycerin and Conversion

In this setup of experiments were conducted at 45°C rpm, 50 ml alcohol,1.0 g catalyst and five different amounts of sunflower oil-150, 200, 250, 300 and 350 ml were placed on the reaction and results obtained are shown in figure 2.

Effect of Alcohol Content

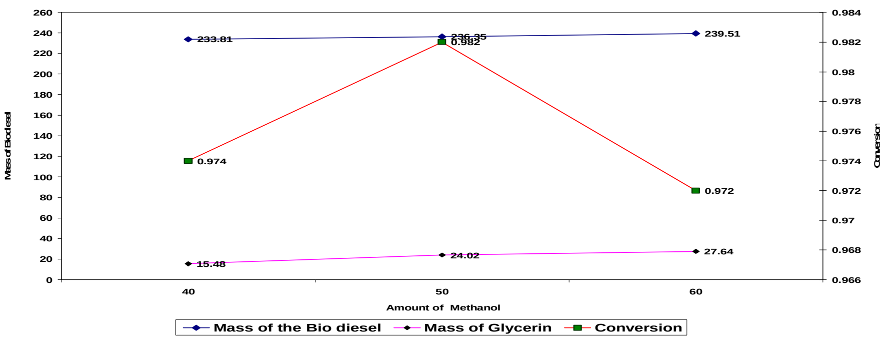


Figure 3: Amount of Methanol vs Mass of Biodiesel, Mass of Glycerin and Conversion

In this setup of experiments were conducted at 45^{o}C, 120rpm, 250 ml alcohol, 1.0 g catalyst and five different amounts of alcohol 40, 50 and 60 ml were placed on the reaction and for corresponding data, the conversion plots are shown in figure 3. Conversion of free fatty acids attained a peak value 98.2% when the oil content is 250 ml and alcohol is 50ml.incresasing the alcohol with 10 ml increment; maintain two variables that are oil content and catalyst are constant. Mass of biodiesel formation slightly increases but the mass glycerin formation is more because some other reaction products will be in the glycerin and it indicates that excess amount of alcohol gives more glycerin formation.

Effect on the Amount of Catalyst

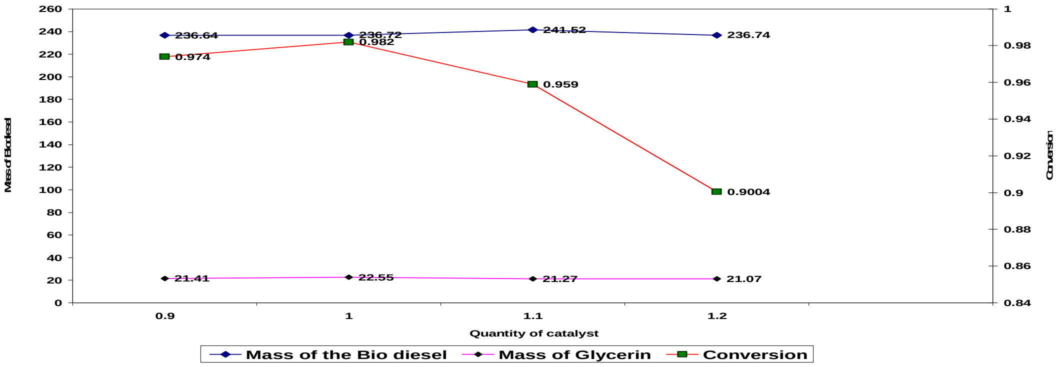


Figure 4: Quantity of Catalyst vs Mass of Biodiesel, Mass of Glycerin and Conversion

In this phase of experimentation, at 45^{o}C, 120 rpm for 20 min,250 ml of oil, 50 ml of alcohol and different amounts of sodium methoxide catalyst-0.9,1.0,1.1 and 1.2 were used the corresponding data obtained are as shown in the figure 4. Mass of biodiesel abruptly changes with increases of 0.1g of catalyst, due to other reaction products were settled in the biodiesel layer and mass of the glycerin steadily increases with increases of catalyst data .Further, it is noticed that the settling time with 0.9g of catalyst is excessively high i.e. 6 days. Slow settling may be attributed to the near equal densities of the two layers. The conversion of free fatty acids changes with the catalyst concentration and it gives maximum conversion at 1g of catalyst and at 0.9 g catalyst; it takes more time for settling nearly 6 to 7 days.

Effect of Reaction Temperature

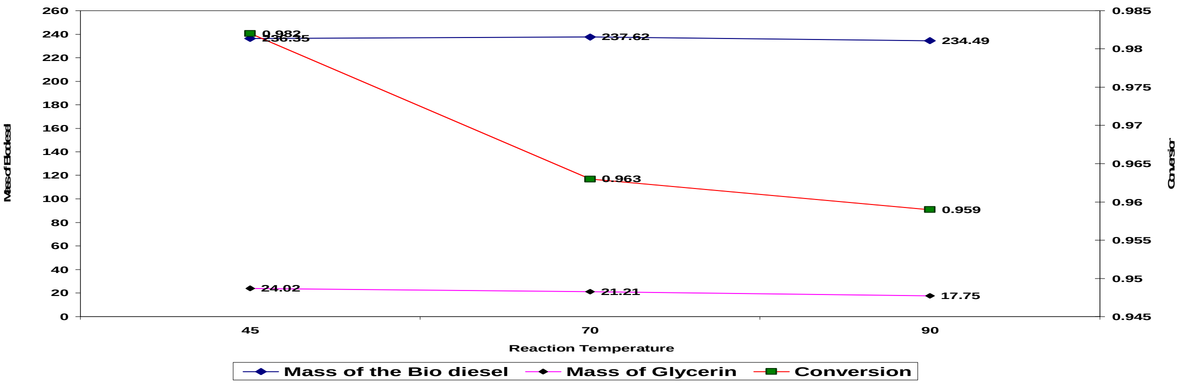


Figure 5: Reaction Temperature vs Mass of Biodiesel, Mass of Glycerin and Conversion

In this run of experiments, were conducting at different temperature 45^{o}C, 70^{o}C and 90^{o}C and 250 ml oil,50 ml alcohol,1.0g catalyst at 120 rpm for 20 min are constant. At 45^{o}C the conversion of free fatty acids obtained is 98.2% and at higher reaction temperature, unpleasant gases will be formed and the conversion of free fatty acids decreases and it

indicates that higher reaction temperatures are not favorable. Mass of biodiesel abruptly changes but mass of glycerin steadily decreases with increasing temperature results are shown in figure 7.

Effect of Reaction Time

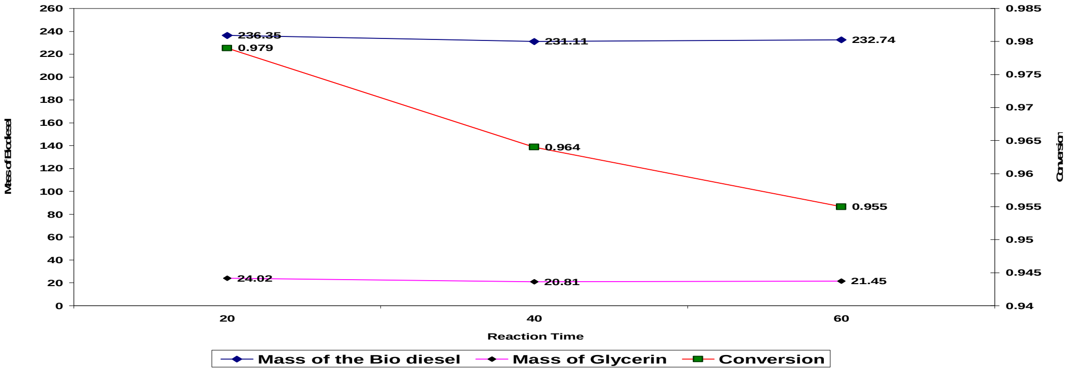


Figure 6: Reaction Time vs Mass of Biodiesel, Mass of Glycerin and Conversion

In this run of experiments, were conducted 45°C, 120 rpm for 20 min, 250 ml oil, 50 ml alcohol and 1.0g catalyst. And at different the reaction time 20, 40 and 60 with increments 20 minutes. At 20 min, the run gives attained maximum conversion of free fatty acids are 98.2% .At higher reaction time, settling time is less but there is no effect on conversion. conversion of free fatty acids plots as shown in figure 8 . It showed that at high reaction times takes less time for settling.

Suitability of Catalyst: In this run of experiments, 250 ml of oil, 50 ml of alcohol and a temperature of 45°C, 120 rpm for 20 min were used in conducting the experiments with different catalysts- sodium methoxide and potassium methoxide. Sodium methoxide catalyst gives more conversion as compared with potassium methoxide. So sodium methoxide is catalyst for production of biodiesel from vegetable oils

Suitability of Various Vegetable Oils: Different vegetables oils-ground nut oil, coconut oil Sun flower oil virgin and used were tried in this run of experiments .the reaction conditions were 45°C and 120 rpm for 20 min, 250 ml oil, 50 ml alcohol and 1.0g catalyst. Conversion of free fatty acids are in the case of virgin oil is the highest at 98.2%. Whereas used Sun flower oil gives 95.4%. And at this reaction conditions coconut oil gives more mass of biodiesel with less glycerin as compared with other vegetable oils and ground nut oil gives homogenous solutions.

CONCLUSIONS

Biodiesel is an alternative to petroleum diesel that can be used in any diesel engine with little or no modification. Biodiesel offer many advantages such as it is renewable, nontoxic biodegradable reduce global warming gas emissions such as $co_{2,}$ sulpher dioxide emissions are eliminated(Biodiesel) contain no sulpher. It can be produce from many vegetable oil or animal fat feed stocks.

There are three basic routes to ester production from oils and fats.

Base catalyzed transesterification of oil with methanol.

Direct acid catalyzed transesterification of oil with methanol.

Conversion of the oil to fatty acids and then to alkyl esters with acids catalysis.

The majority of the alkyl esters produce today is done with Base catalyzed reactions because it is the most

economic for several reasons. Low temperature (150^0F) and pressure (20 psi) processing high conversion (98.2%) with minimal side reactions and reaction time. Direct conversion to methyl ester with no intermediate steps. Exotic materials of constructions are not necessary. In the present work production of biodiesel with different oils, Sun flower oil is suitable alternative to perform transesterification reaction with good results. Catalyst (1.25 ml of methanol and 0.25ml NaoH) 1ml for 250 ml of Sun flower oil shows both better final conversion and a good reaction rate at operational conditions in this work. This composition of catalyst gives better conversion that the other amount of catalyst. For changes on the temperature, even though this is an effect we are studying at the movement; final conversion follows an exothermic behavior. So here unpleasant gases formed.

Variation on the amount of alcohol show not great effect on the reaction, even though when more alcohol is added to the system.50ml of alcohol gives better conversion. Variation on the reaction time, settling rate is faster by increasing the reaction time. There is no effect on conversion 20 min at 120 rpm gives better conversion.

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